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<b>(21) International Application Number:</b> PCT/NL97/00244 <b>(22) International Filing Date:</b> 1 May 1997 (01.05.97)  <b>(30) Priority Data:</b> 96201112.8 3 May 1996 (03.05.96) EP (34) Countries for which the regional or international application was filed: NL et al.  <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> RENKEMA, Jacob [NL/NL]; Heer Ottostraat 25, NL-6121 NB Born (NL). VAN TOL, Maurits, Frederik, Hendrik [NL/NL]; Scheiff. van Merodestraat 17, NL-6141 BC Sittard (NL). WIND-MULLER, Peter, Jozef, Hubert [NL/NL]; Rooseveltstraat 16, NL-6374 JC Landgraaf (NL). VAN BEEK, Johannes, Antonius, Maria [NL/US]; 75 Tyrella Court, Mountain View, CA 94043 (US).  <b>(74) Agent:</b> SCHELTUS, Irma; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> With international search report.
<b>(54) Title:</b> PROCESS FOR THE PREPARATION OF A TERPOLYMER OF ETHYLENE, AN $\alpha$ -OLEFIN AND A DIENE		
<b>(57) Abstract</b>  The invention relates to process for the preparation of a terpolymer of ethylene, an $\alpha$ -olefin and a diene, and which comprises the use of a transition metal complex and a co-catalyst. The invention is characterized in that the polymerization is conducted using a transition metal complex consisting of a reduced transition metal complex, chosen from groups 4-6 of the Periodic Table of the Elements, with a multidentate monoanionic ligand and with two monoanionic ligands, at a temperature of between -10 and 220 °C. In particular the reduced transition metal in the complex is titanium (Ti).		

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PROCESS FOR THE PREPARATION OF A TERPOLYMER OF  
ETHYLENE, AN  $\alpha$ -OLEFIN AND A DIENE

5

BACKGROUND OF THE INVENTION

10 The invention relates to a process for the preparation of a terpolymer of ethylene, an  $\alpha$ -olefin and a diene, with an ethylene content of between about 20 and about 90 weight %, and a diene content of up to 30 weight %, with a catalyst composition comprising a transition metal complex and a co-catalyst.

15 Here and hereinafter the terpolymer will also be referred to as to "EADM" (ethylene  $\alpha$ -olefin diene monomer) polymer; in case the  $\alpha$ -olefin is propylene, the terpolymer will also be referred to as to "EPDM" (ethylene propylene diene monomer).

20 A process for the preparation of an EADM is known from EP-A-347,129, in which a cyclopentadiene based transition metal complex (in combination with a co-catalyst) is used as a catalyst. A disadvantage of a process according to EP-A-347,129 is that it has to be conducted at relatively  
25 low temperatures, which causes the process to be less attractive from an economical point of view. There is a need for a process to be conducted at higher temperatures; on the other hand the pressure should preferably not be too high as otherwise the costs for such a high pressure process could  
30 undo the advantages of a high temperature process.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to solve the aforementioned problems associated  
35 with the related art as well as to address the need expressed above.

In the process according to the present invention, it is an object to prepare terpolymers having an ethylene content of about 20-90 weight %, a diene content of up to about 30 weight %, and an  $\alpha$ -olefin.

5 It is a further object of the invention to prepare such terpolymers at higher temperatures than conventional processes, for instance up to about 220°C.

Another object of the present invention is the preparation of such terpolymers having an average molecular  
10 weight of as low as 10g/mol.

These and other objects, features, and advantages of the present invention will become apparent from the following detailed description when taken in conjunction with the accompanying drawings which illustrate, by way of  
15 example, the principles of the present invention.

In accordance with the principles of the present invention, these objects and others are obtained by providing a process for the preparation of a terpolymer of ethylene, an  $\alpha$ -olefin and a diene, in the presence of the present catalyst  
20 composition.

The process according to the invention is characterized in that the polymerization is conducted at a temperature of between about -10°C to about 220°C, and preferably between about 75°C and about 220°C, under the  
25 influence of a transition metal complex of the structure shown below in Formula (I). The catalyst composition includes at least one complex comprising a reduced valency transition metal (M) selected from groups 4-6 of the Periodic Table of Elements, a multidentate monoanionic ligand (X), two  
30 monoanionic ligands (L), and, optionally, additional ligands (K). More specifically, the complex of the catalyst composition of the present invention is represented by the following formula (I):



wherein the symbols have the following meanings:

- M a reduced transition metal selected from group 4, 5 or 6  
 10 of the Periodic Table of Elements;
- X a multidentate monoanionic ligand represented by the  
 formula:  $(\text{Ar}-\text{R}_t)_s\text{Y}(-\text{R}_t-\text{DR}'_n)_q$ ;
- Y a cyclopentadienyl, amido  $(-\text{NR}'-)$ , or phosphido group  
 15  $(-\text{PR}'-)$ , which is bonded to the reduced transition metal  
 M;
- R at least one member selected from the group consisting  
 of (i) a connecting group between the Y group and the  
 $\text{DR}'_n$  group and (ii) a connecting group between the Y  
 group and the Ar group, wherein when the ligand X  
 20 contains more than one R group, the R groups can be  
 identical to or different from each other;
- D an electron-donating hetero atom selected from group 15  
 or 16 of the Periodic Table of Elements;
- R' a substituent selected from the group consisting of a  
 25 hydrogen, hydrocarbon radical and hetero atom-containing  
 moiety, except that R' cannot be hydrogen when R' is  
 directly bonded to the electron-donating hetero atom D,  
 wherein when the multidentate monoanionic ligand X  
 contains more than one substituent R', the substituents  
 30 R' can be identical or different from each other;
- Ar an electron-donating aryl group;
- L a monoanionic ligand bonded to the reduced transition  
 metal M, wherein the monoanionic ligand L is not a  
 ligand comprising a cyclopentadienyl, amido  $(-\text{NR}'-)$ , or  
 35 phosphido  $(-\text{PR}'-)$  group, and wherein the monoanionic  
 ligands L can be identical or different from each other;

- K a neutral or anionic ligand bonded to the reduced transition metal M, wherein when the transition metal complex contains more than one ligand K, the ligands K can be identical or different from each other;
- 5 m is the number of K ligands, wherein when the K ligand is an anionic ligand m is 0 for  $M^{3+}$ , m is 1 for  $M^{4+}$ , and m is 2 for  $M^{5+}$ , and when K is a neutral ligand m increases by one for each neutral K ligand;
- 10 n the number of the R' groups bonded to the electron-donating hetero atom D, wherein when D is selected from group 15 of the Periodic Table of Elements n is 2, and when D is selected from group 16 of the Periodic Table of Elements n is 1;
- 15 q,s q and s are the number of  $(-R_t-DR'_n)$  groups and  $(Ar-R_t-)$  groups bonded to group Y, respectively, wherein  $q + s$  is an integer not less than 1; and
- t the number of R groups connecting each of (i) the Y and Ar groups and (ii) the Y and  $DR'_n$  groups, wherein t is selected independently as 0 or 1.

20

A few non-limiting examples of transition metal complexes according to the invention are presented below in Table 1.

25

#### BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate the present invention. In such drawings:

30 FIG. 1 is a schematic view of a cationic active site of a trivalent catalyst complex in accordance with an embodiment of the present invention; and

FIG. 2 is a schematic view of a neutral active site of a trivalent catalyst complex of a dianionic ligand of a conventional catalyst complex according to WO-A-93/19104.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has surprisingly been found that a transition metal complex of formula (I) is capable of facilitating preparation of EADM's at the indicated temperature level, whereas other known catalysts for these types of polymerisation do not produce those polymers at this temperature level (they are only active at temperatures well below 100°C; see the examples in the referenced EP-A-347,129).

The process according to the present invention is suitable for the preparation of EADM's having an  $M_n$  (the number-average molecular weight as determined by SEC-DV (Size Exclusion Chromatography/Differential Viscometry combination)), of as low as 100 (g/mol). The temperature at which the polymerization is performed is one of the parameters to control the value of  $M_n$ . In principle any EADM can be made with an  $M_n$  between about 100 and about 500,000.

The polymers also have an ethylene content generally of between about 20 and about 90 weight %. The polymers can be amorphous, being products with an ethylene content of between 30 and 70 weight %, or can be semicrystalline.

As an example, EADM's with a molecular weight  $M_n$  between 100 and 30,000 are prepared in a polymerization process at temperatures between 135 and 220°C; EADM's with a molecular weight  $M_n$  between 20,000 and 100,000 are preferably prepared in a polymerization process at a temperature between 115 and 180°C.

The pressure at which the polymerization is conducted is in general below 100 MPa. Pressures up to 10 MPa are in several cases sufficient enough for a good catalytic activity.

Other processes known in the art to produce low molecular weight EADM's either start from high molecular weight products which are broken down in molecular weight

(e.g. by shearing) or by using, during the polymerization, an extreme amount of chain regulators (e.a. hydrogen or diethylzinc) for keeping the molecular weight low.

The process according to the invention is suitable for the preparation of low molecular weight semi-crystalline or of amorphous polymers based on ethene, an  $\alpha$ -olefin and a diene. It is also suitable, and preferably used for the preparation of high molecular weight EADM's; that is to say, polymers with a  $M_n$  of at least about 50,000 or with a Mooney viscosity ( $ML_{1+4}$ , 125°C, according to ASTM D1646) of 10-150.

Besides the ethylene, the polymer according to the invention comprises one or more  $\alpha$ -olefins. In general, such an  $\alpha$ -olefin contains 3-25 carbon atoms (although higher  $\alpha$ -olefins are also allowable); more preferably, the  $\alpha$ -olefin contains 3-10 carbon atoms. The  $\alpha$ -olefine has preferably been selected from the group consisting of propylene, butene, isobutene, pentene, 4-methyl pentene, hexene, octene and ( $\alpha$ -methyl) styrene. More preferably, the  $\alpha$ -olefine is propylene, 1-butene, 1-hexene or 1-octene, styrene, or ( $\alpha$ -methyl)styrene. Most preferred is the  $\alpha$ -olefin propylene, resulting in the preparation of EPDM.

The polymer also comprises one or more dienes. The diene in the polymer according to the invention is a polyunsaturated compound; it contains at least two C=C bonds and may be aliphatic as well as alicyclic. Aliphatic polyunsaturated compounds in general contain 3 to 20 carbon atoms, while the double bonds may be conjugated as well as, preferably, non-conjugated. Examples of such compounds are: 1,3-butadiene, isoprene, 2,3-dimethyl butadiene-1,3, 2-ethyl butadiene-1,3, piperylene, myrcene, allenes, 1,2-butadiene, 1,4,9-decatrienes, 1,4-hexadiene, octadiene, 1,5-hexadiene and 4-methyl hexadiene-1,4.

Alicyclic polyunsaturated compounds, with or without a bridging group, may be either monocyclic or polycyclic. Examples of such compounds are norbornadiene and



its alkyl derivatives; the alkylidene norbornenes, in particular the 5-alkylidene norbornenes-2, in which the alkylidene group contains 1 to 20, by preference 1 to 8 carbon atoms; the alkenyl norbornenes, in particular the 5-alkenyl norbornenes-2, in which the alkenyl group contains 2 to 20, by preference 2 to 10 carbon atoms, for instance vinyl norbornene, 5-(2'-methyl-2'-butenyl)-norbornene-2 and 5-(3'-methyl-2'-butenyl)-norbornene-2; dicyclopentadiene and the polyunsaturated compounds of bicyclo-(2,2,1)-heptane, bicyclo-(2,2,2)-octane, bicyclo(3,2,1)-octane and bicyclo-(3,2,2)-nonane, with at least one of the rings being unsaturated. Further, compounds such as 4,7,8,9-tetrahydroindene and isopropylidene tetrahydroindene can be used. In particular, dicyclopentadiene, ethylidene norbornene, vinyl norbornene, or hexadiene are used. Mixtures of the compounds mentioned in the foregoing may also be used.

The diene is present in the polymer in quantities of up to 30 weight %, typically however up to 10-15 weight %. Even more preferred is an amount of diene in the copolymer of 1-10 weight %, specifically between 2 and 8 weight %.

Various components (groups) of the transition metal complex are discussed below in more detail.

(a) The Transition Metal (M)

The transition metal in the complex is selected from groups 4-6 of the Periodic Table of Elements. As referred to herein, all references to the Periodic Table of Elements mean the version set forth in the new IUPAC notation found on the inside of the cover of the Handbook of Chemistry and Physics, 70th edition, 1989/1990, the complete disclosure of which is incorporated herein by reference. More preferably, the transition metal is selected from group 4 of the Periodic Table of Elements, and most preferably is titanium (Ti).

The transition metal is present in reduced form in the complex, which means that the transition metal is in a reduced oxidation state. As referred to herein, "reduced oxidation state" means an oxidation state which is greater than zero but lower than the highest possible oxidation state of the metal (for example, the reduced oxidation state is at most  $M^{3+}$  for a transition metal of group 4, at most  $M^{4+}$  for a transition metal of group 5 and at most  $M^{5+}$  for a transition metal of group 6).

10

(b) The X Ligand

The X ligand is a multidentate monoanionic ligand represented by the formula:  $(Ar-R_t-)_nY(-R_t-DR'_n)_q$ .

As referred to herein, a multidentate monoanionic ligand is bonded with a covalent bond to the reduced transition metal (M) at one site (the anionic site, Y) and is bonded either (i) with a coordinate bond to the transition metal at one other site (bidentate) or (ii) with a plurality of coordinate bonds at several other sites (tridentate, tetradentate, etc.). Such coordinate bonding can take place, for example, via the D heteroatom or Ar group(s). Examples of tridentate monoanionic ligands include, without limitation,  $Y-R_t-DR'_{n-1}-R_t-DR'_n$  and  $Y(-R-DR'_n)_2$ . It is noted, however, that heteroatom(s) or aryl substituent(s) can be present on the Y group without coordinately bonding to the reduced transition metal M, so long as at least one coordinate bond is formed between an electron-donating group D or an electron donating Ar group and the reduced transition metal M.

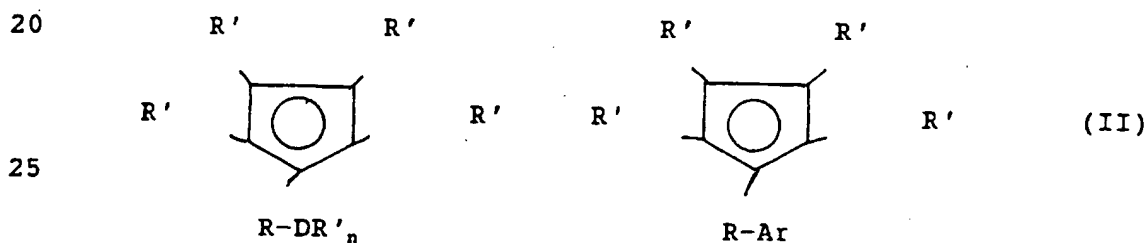
R represents a connecting or bridging group between the  $DR'_n$  and Y, and/or between the electron-donating aryl (Ar) group and Y. Since R is optional, "t" can be zero. The R group is discussed below in paragraph (d) in more detail.

## (c) The Y Group

The Y group of the multidentate monoanionic ligand (X) is preferably a cyclopentadienyl, amido ( $-NR'-$ ), or phosphido ( $-PR'-$ ) group.

5 Most preferably, the Y group is a cyclopentadienyl ligand (Cp group). As referred to herein, the term cyclopentadienyl group encompasses substituted cyclopentadienyl groups such as indenyl, fluorenyl, and benzoindenyl groups, and other polycyclic aromatics  
 10 containing at least one 5-member dienyli ring, so long as at least one of the substituents of the Cp group is an  $R_t-DR'_n$  group or  $R_t-Ar$  group that replaces one of the hydrogens bonded to the five-member ring of the Cp group via an exocyclic substitution.

15 Examples of a multidentate monoanionic ligand with a Cp group as the Y group (or ligand) include the following (with the ( $-R_t-DR'_n$ ) or ( $Ar-R_t-$ ) substituent on the ring):

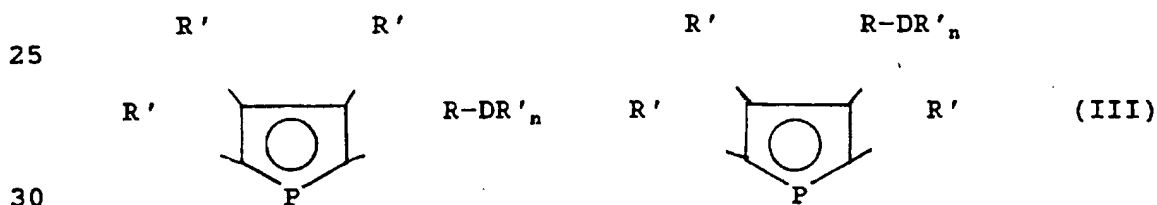


30 The Y group can also be a hetero cyclopentadienyl group. As referred to herein, a hetero cyclopentadienyl group means a hetero ligand derived from a cyclopentadienyl group, but in which at least one of the atoms defining the five-  
 35 member ring structure of the cyclopentadienyl is replaced with a hetero atom via an endocyclic substitution. The hetero Cp group also includes at least one  $R_t-DR'_n$  group or  $R_t-Ar$  group that replaces one of the hydrogens bonded to the five-member ring of the Cp group via an exocyclic substitution. As

with the Cp group, as referred to herein the hetero Cp group encompasses indenyl, fluorenyl, and benzoindenyl groups, and other polycyclic aromatics containing at least one 5-member dienyli ring, so long as at least one of the substituents of the hetero Cp group is an  $R_t-DR'_n$  group or  $R_t-Ar$  group that replaces one of the hydrogens bonded to the five-member ring of the hetero Cp group via an exocyclic substitution.

The hetero atom can be selected from group 14, 15 or 16 of the Periodic Table of Elements. If there is more than one hetero atom present in the five-member ring, these hetero atoms can be either the same or different from each other. More preferably, the hetero atom(s) is/are selected from group 15, and still more preferably the hetero atom(s) selected is/are phosphorus.

By way of illustration and without limitation, representative hetero ligands of the X group that can be practiced in accordance with the present invention are hetero cyclopentadienyl groups having the following structures, in which the hetero cyclopentadienyl contains one phosphorus atom (i.e., the hetero atom) substituted in the five-member ring:

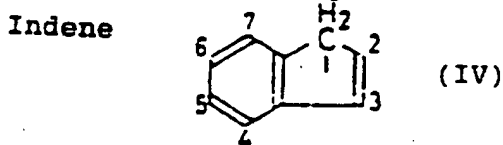


35 It is noted that, generally, the transition metal group M is bonded to the Cp group via an  $\eta^5$  bond.

The other  $R'$  exocyclic substituents (shown in formula (III)) on the ring of the hetero Cp group can be of the same type as those present on the Cp group, as

represented in formula (II). As in formula (II), at least one of the exocyclic substituents on the five-member ring of the hetero cyclopentadienyl group of formula (III) is the  $R_t-DR'_n$  group or the  $R_t-Ar$  group.

5           The numeration of the substitution sites of the indenyl group is in general and in the present description based on the IUPAC Nomenclature of Organic Chemistry 1979, rule A 21.1. The numeration of the substituent sites for indene is shown below. This numeration is analogous for an  
10 indenyl group:



15           The Y group can also be an amido ( $-NR'-$ ) group or a phosphido ( $-PR'-$ ) group. In these alternative embodiments, the Y group contains nitrogen (N) or phosphorus (P) and is bonded covalently to the transition metal M as well as to the  
20 (optional) R group of the ( $-R_t-DR'_n$ ) or ( $Ar-R_t-$ ) substituent.

(d)           The R Group

          The R group is optional, such that it can be absent from the X group. Where the R group is absent, the  $DR'_n$  or Ar group is bonded directly to the Y group (that is, the  $DR'_n$  or Ar group is bonded directly to the Cp, amido, or phosphido group). The presence or absence of an R group between each of the  $DR'_n$  groups and/or Ar groups is independent.

          Where at least one of the R groups is present, each  
30 of the R group constitutes the connecting bond between, on the one hand the Y group, and on the other hand the  $DR'_n$  group or the Ar group. The presence and size of the R group determines the accessibility of the transition metal M relative to the  $DR'_n$  or Ar group, which gives the desired  
35 intramolecular coordination. If the R group (or bridge) is too short or absent, the donor may not coordinate well due to

ring tension. The R groups are each selected independently, and can generally be, for example, a hydrocarbon group with 1-20 carbon atoms (e.g., alkylidene, arylidene, aryl alkylidene, etc.). Specific examples of such R groups  
5 include, without limitation, methylene, ethylene, propylene, butylene, phenylene, whether or not with a substituted side chain. Preferably, the R group has the following structure:



10

where  $p = 1-4$ . The  $R'$  groups of formula (IV) can each be selected independently, and can be the same as the  $R'$  groups defined below in paragraph (g).

In addition to carbon, the main chain of the R  
15 group can also contain silicon or germanium. Examples of such R groups are: dialkyl silylene ( $-SiR'_2-$ ), dialkyl germylene ( $-GeR'_2-$ ), tetra-alkyl silylene ( $-SiR'_2-SiR'_2-$ ), or tetraalkyl silaethylene ( $-SiR'_2CR'_2-$ ). The alkyl groups in  
20 such a group preferably have 1-4 carbon atoms and more preferably are a methyl or ethyl group.

(e) The  $DR'_n$  Group

This donor group consists of an electron-donating hetero atom D, selected from group 15 or 16 of the Periodic  
25 Table of Elements, and one or more substituents  $R'$  bonded to D. The number (n) of  $R'$  groups is determined by the nature of the hetero atom D, insofar as n being 2 if D is selected from group 15 and n being 1 if D is selected from group 16. The  $R'$  substituents bonded to D can each be selected independently,  
30 and can be the same as the  $R'$  groups defined below in paragraph (g), with the exception that the  $R'$  substituent bonded to D cannot be hydrogen.

The hetero atom D is preferably selected from the group consisting of nitrogen (N), oxygen (O), phosphorus (P)  
35 and sulphur (S); more preferably, the hetero atom is nitrogen

(N). Preferably, the R' group is an alkyl, more preferably an n-alkyl group having 1-20 carbon atoms, and most preferably an n-alkyl having 1-8 carbon atoms. It is further possible for two R' groups in the DR'<sub>n</sub> group to be connected with each other to form a ring-shaped structure (so that the DR'<sub>n</sub> group can be, for example, a pyrrolidinyl group). The DR'<sub>n</sub> group can form coordinate bonds with the transition metal M.

(f) The Ar Group

The electron-donating group (or donor) selected can also be an aryl group (C<sub>6</sub>R'<sub>5</sub>), such as phenyl, tolyl, xylyl, mesityl, cumenyl, tetramethyl phenyl, pentamethyl phenyl, a polycyclic group such as triphenylmethane, etc. The electron-donating group D of formula (I) cannot, however, be a substituted Cp group, such as an indenyl, benzoindenyl, or fluorenyl group.

The coordination of this Ar group in relation to the transition metal M can vary from  $\eta^1$  to  $\eta^6$ .

(g) The R' Group

The R' groups may each separately be hydrogen or a hydrocarbon radical with 1-20 carbon atoms (e.g. alkyl, aryl, aryl alkyl and the like as shown in Table 1). Examples of alkyl groups are methyl, ethyl, propyl, butyl, hexyl and decyl. Examples of aryl groups are phenyl, mesityl, tolyl and cumenyl. Examples of aryl alkyl groups are benzyl, pentamethylbenzyl, xylyl, styryl and trityl. Examples of other R' groups are halides, such as chloride, bromide, fluoride and iodide, methoxy, ethoxy and phenoxy.

Also, two adjacent hydrocarbon radicals of the Y group can be connected with each other to define a ring system; therefore the Y group can be an indenyl, a fluorenyl or a benzoindenyl group. The indenyl, fluorenyl, and/or benzoindenyl can contain one or more R' groups as substituents. R' can also be a substituent which instead of or in addition to carbon

and/or hydrogen can comprise one or more hetero atoms of groups 14-16 of the Periodic Table of Elements. Thus, a substituent can be, for example, a Si-containing group, such as  $\text{Si}(\text{CH}_3)_3$ .

5

(h) The L Group

The transition metal complex contains two monoanionic ligands L bonded to the transition metal M. Examples of the L group ligands, which can be identical or different, include, without limitation, the following: a hydrogen atom; a halogen atom; an alkyl, aryl or aryl alkyl group; an alkoxy or aryloxy group; a group comprising a hetero atom selected from group 15 or 16 of the Periodic Table of Elements, including, by way of example, (i) a sulphur compound, such as sulphite, sulphate, thiol, sulphonate, and thioalkyl, and (ii) a phosphorus compound, such as phosphite, and phosphate. The two L groups can also be connected with each other to form a dianionic bidentate ring system.

20 These and other ligands can be tested for their suitability by means of simple experiments by one skilled in the art.

Preferably, L is a halide and/or an alkyl or aryl group; more preferably, L is a Cl group and/or a  $\text{C}_1\text{-C}_4$  alkyl or a benzyl group. The L group, however, cannot be a Cp, amido, or phosphido group. In other words, L cannot be one of the Y groups.

(i) The K Ligand

30 The K ligand is a neutral or anionic group bonded to the transition metal M. The K group is a neutral or anionic ligand bonded to M. When K is a neutral ligand K may be absent, but when K is monoanionic, the following holds for  $K_m$ :

35  $m = 0$  for  $M^{3+}$



$m = 1$  for  $M^{4+}$

$m = 2$  for  $M^{5+}$

On the other hand, neutral K ligands, which by definition are not anionic, are not subject to the same rule.

5 Therefore, for each neutral K ligand, the value of  $m$  (i.e., the number of total K ligands) is one higher than the value stated above for a complex having all monoanionic K ligands.

The K ligand can be a ligand as described above for the L group or a Cp group ( $-C_5R'_5$ ), an amido group ( $-NR'_2$ ) or  
10 a phosphido group ( $-PR'_2$ ). The K group can also be a neutral ligand such as an ether, an amine, a phosphine, a thioether, among others.

If two K groups are present, the two K groups can be connected with each other via an R group to form a  
15 bidentate ring system.

As can also be seen from formula (I), the X group of the complex contains a Y group to which are linked one or more donor groups (the Ar group(s) and/or  $DR'_n$  group(s)) via, optionally, an R group. The number of donor groups linked to  
20 the Y group is at least one and at most the number of substitution sites present on a Y group.

With reference, by way of example, to the structure according to formula (II), at least one substitution site on a Cp group is made by an  $R_t$ -Ar group or by an  $R_t$ - $DR'_n$  group  
25 (in which case  $q + s = 1$ ). If all the  $R'$  groups in formula (II) were  $R_t$ -Ar groups,  $R_t$ - $DR'_n$  groups, or any combination thereof, the value of  $(q + s)$  would be 5.

One preferred embodiment of the catalyst composition according to the present invention comprises a  
30 transition metal complex in which a bidentate/monoanionic ligand is present and in which the reduced transition metal has been selected from group 4 of the Periodic Table of Elements and has an oxidation state of +3.

In this case, the catalyst composition according to the invention comprises a transition metal complex represented by formula (V):



where the symbols have the same meaning as described above for formula (I) and where M(III) is a transition metal selected from group 4 of the Periodic Table of Elements and is in oxidation state 3+.

Such a transition metal complex has no anionic K ligands (for an anionic K,  $m = 0$  in case of  $\text{M}^{3+}$ ).

It should be pointed out that in WO-A-93/19104, transition metal complexes are described in which a group 4 transition metal in a reduced oxidation state (3+) is present. The complexes described in WO-A-93/19104 have the general formula:



The Y group in this formula (VI) is a hetero atom, such as phosphorus, oxygen, sulfur, or nitrogen bonded covalently to the transition metal M (see p. 2 of WO-A-93/19104). This means that the  $\text{Cp}_a(\text{ZY})_b$  group is of a dianionic nature, and has the anionic charges residing formerly on the Cp and Y groups. Accordingly, the  $\text{Cp}_a(\text{ZY})_b$  group of formula (VI) contains two covalent bonds: the first being between the 5-member ring of the Cp group and the transition metal M, and the second being between the Y group and the transition metal. By contrast, the X group in the complex according to the present invention is of a monoanionic nature, such that a covalent bond is present between the Y group (e.g., the Cp

group) and transition metal, and a coordinate bond can be present between the transition metal M and one or more of the ( $\text{Ar-R}_t$ -) and ( $-\text{R}_t\text{-DR}'_n$ ) groups. This changes the nature of the transition metal complex and consequently the nature of the catalyst that is active in the polymerization. As referred to herein, a coordinate bond is a bond (e.g.,  $\text{H}_3\text{N-BH}_3$ ) which when broken, yields either (i) two species without net charge and without unpaired electrons (e.g.,  $\text{H}_3\text{N:}$  and  $\text{BH}_3$ ) or (ii) two species with net charge and with unpaired electrons (e.g.,  $\text{H}_3\text{N}^+$  and  $\text{BH}_3^-$ ). On the other hand, as referred to herein, a covalent bond is a bond (e.g.,  $\text{CH}_3\text{-CH}_3$ ) which when broken yields either (i) two species without net charge and with unpaired electrons (e.g.,  $\text{CH}_3\cdot$  and  $\text{CH}_3\cdot$ ) or (ii) two species with net charges and without unpaired electrons (e.g.,  $\text{CH}_3^+$  and  $\text{CH}_3^-$ ). A discussion of coordinate and covalent bonding is set forth in Haaland et al. (Angew. Chem Int. Ed. Eng. Vol. 28, 1989, p. 992), the complete disclosure of which is incorporated herein by reference.

The following explanation is proposed, although it is noted that the present invention is in no way limited to this theory.

Referring now more particularly to FIG. 2, the transition metal complexes described in WO-A-93/19104 are ionic after interaction with the co-catalyst. However, the transition metal complex according to WO-A-93/19104 that is active in the polymerization contains an overall neutral charge (on the basis of the assumption that the polymerizing transition metal complex comprises, a M(III) transition metal, one dianionic ligand and one growing monoanionic polymer chain (POL)). By contrast, as shown in FIG. 1, the polymerization active transition metal complex of the catalyst composition according to the present invention is of a cationic nature (on the basis of the assumption that the polymerizing transition metal complex - based on the formula (V) structure - comprises, a M(III) transition metal, one

monoanionic bidentate ligand and on growing monoanionic polymer chain (POL)).

Transition metal complexes in which the transition metal is in a reduced oxidation state, but have the following structure:



are generally not active in co-polymerization reactions. It is precisely the presence, in the transition metal complex of the present invention, of the DR'<sub>n</sub> or Ar group (the donor), optionally bonded to the Y group by means of the R group, that gives a stable transition metal complex suitable for polymerization.

Such an intramolecular donor is to be preferred over an external (intermolecular) donor on account of the fact that the former shows a stronger and more stable coordination with the transition metal complex.

It will be appreciated that the catalyst system may also be formed in situ if the components thereof are added directly to the polymerization reactor system and a solvent or diluent, including liquid monomer, is used in said polymerization reactor.

The catalyst composition of the present invention also contains a co-catalyst. For example, the co-catalyst can be an organometallic compound. The metal of the organometallic compound can be selected from group 1, 2, 12 or 13 of the Periodic Table of Elements. Suitable metals include, for example and without limitation, sodium, lithium, zinc, magnesium, and aluminum, with aluminum being preferred. At least one hydrocarbon radical is bonded directly to the metal to provide a carbon-metal bond. The hydrocarbon group used in such compounds preferably contains 1-30, more preferably 1-10 carbon atoms. Examples of suitable compounds include, without limitation, amyl sodium, butyl lithium,

diethyl zinc, butyl magnesium chloride, and dibutyl magnesium. Preference is given to organoaluminium compounds, including, for example and without limitation, the following: trialkyl aluminum compounds, such as triethyl aluminum and tri-isobutyl aluminum; alkyl aluminum hydrides, such as di-isobutyl aluminum hydride; alkylalkoxy organoaluminium compounds; and halogen-containing organoaluminium compounds, such as diethyl aluminum chloride, diisobutyl aluminum chloride, and ethyl aluminum sesquichloride. Preferably, linear or cyclic aluminoxanes are selected as the organoaluminium compound.

In addition or as an alternative to the organometallic compounds as the co-catalyst, the catalyst composition of the present invention can include a compound which contains or yields in a reaction with the transition metal complex of the present invention a non-coordinating or poorly coordinating anion. Such compounds have been described for instance in EP-A-426,637, the complete disclosure of which is incorporated herein by reference. Such an anion is bonded sufficiently unstably such that it is replaced by an unsaturated monomer during the co-polymerization. Such compounds are also mentioned in EP-A-277,003 and EP-A-277,004, the complete disclosures of which are incorporated herein by reference. Such a compound preferably contains a triaryl borane or a tetraaryl borate or an aluminum equivalent thereof. Examples of suitable co-catalyst compounds include, without limitation, the following:

- dimethyl anilinium tetrakis (pentafluorophenyl) borate  $[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{H}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ ;
- 30 - dimethyl anilinium bis (7,8-dicarbaundecaborate)-cobaltate (III);
- tri(n-butyl)ammonium tetraphenyl borate;
- triphenylcarbenium tetrakis (pentafluorophenyl) borate;
- dimethylanilinium tetraphenyl borate;
- 35 - tris(pentafluorophenyl) borane; and

- tetrakis(pentafluorophenyl) borate.

If the above-mentioned non-coordinating or poorly coordinating anion is used, it is preferable for the transition metal complex to be alkylated (that is, the L group is an alkyl group). As described for instance in EP-A-500,944, the complete disclosure of which is incorporated herein by reference, the reaction product of a halogenated transition metal complex and an organometallic compound, such as for instance triethyl aluminum (TEA), can also be used.

The molar ratio of the co-catalyst relative to the transition metal complex, in case an organometallic compound is selected as the co-catalyst, usually is in a range of from about 1:1 to about 10,000:1, and preferably is in a range of from about 1:1 to about 2,500:1. If a compound containing or yielding a non-coordinating or poorly coordinating anion is selected as co-catalyst, the molar ratio usually is in a range of from about 1:100 to about 1,000:1, and preferably is in a range of from about 1:2 to about 250:1.

As a person skilled in the art would be aware, the transition metal complex as well as the co-catalyst can be present in the catalyst composition as a single component or as a mixture of several components. For instance, a mixture may be desired where there is a need to influence the molecular properties of the polymer, such as molecular weight and in particular molecular weight distribution.

The catalyst composition used in the process according to the invention can be used supported as well as non-supported. The supported catalysts are used mainly in gas phase and slurry processes. The carrier used may be any carrier known as carrier material for catalysts, for instance  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{MgCl}_2$ , zeolites, mineral clays, inorganic oxides such as talc, silica-alumina, inorganic hydroxides, phosphates, sulphates, etc. or resinous support materials such as polyolefins, including polystyrene, or mixtures thereof. Suitable brands of silane carriers are MAO/ $\text{SiO}_2$ , from

Witco, based on PQMS3040 SiO<sub>2</sub> and SiO<sub>2</sub> Grace Davison under code W952. The carrier may be used as such, or be modified, for example by silanes, aluminiumalkyls, aluminoxanes, and others. The catalyst composition may also be prepared by in-situ methods.

Polymerization can be effected in a known manner, in the gas phase as well as in a liquid reaction medium. In the latter case, both solution and suspension polymerization are suitable, while the quantity of transition metal to be used generally is such that its concentration in the dispersion agent amounts to  $10^{-8}$  -  $10^{-3}$  mol/l, preferably  $10^{-7}$  -  $10^{-4}$  mol/l.

Any liquid that is inert relative to the catalyst system can be used as a dispersion agent in the polymerization. One or more saturated, straight or branched aliphatic hydrocarbons, such as butanes, pentanes, hexanes, heptanes, pentamethyl heptane or mineral oil fractions such as light or regular petrol, naphtha, kerosine or gas oil are suitable for that purpose. Aromatic hydrocarbons, for instance benzene and toluene, can be used, but because of their cost and environmental hazards it is preferred not to use such solvents for production on a commercial scale.

In polymerization processes on a commercial scale, it is preferred, therefore, to use as a solvent the low-priced aliphatic hydrocarbons, liquid monomers, or mixtures thereof, as marketed by the petrochemical industry. If an aliphatic hydrocarbon is used as a solvent, the solvent may yet contain minor quantities of aromatic hydrocarbon, for instance toluene. Thus, if for instance methyl aluminoxane (MAO) is used as co-catalyst, toluene can be used as solvent for the MAO in order to supply the MAO in dissolved form to the polymerization reactor. Drying or purification is desirable if such solvents are used; this can be done without problems by the average person skilled in the art.

If the polymerization is carried out under pressure, the yield of polymer can be increased additionally, resulting in an even lower catalyst residue content. Chain regulators (such as hydrogen or diethyl zinc) can be used to control the molecular weight and the amount of unsaturation of the resulting EADM. Preference is given to hydrogen as the chain regulator.

The polymerization can also be performed in several steps, in series as well as in parallel. If required, the catalyst composition, temperature, hydrogen concentration, pressure, residence time, etc. may be varied from step to step. In this way it is also possible to obtain products with a wide molecular weight distribution.

The polymer solution resulting from the polymerization can be worked up by a method known per se. The polymer can be isolated by solution polymerization by methods known in the art. In general, the catalyst is de-activated at some point during the processing of the polymer. The de-activation is also effected in a manner known per se, e.g. by means of water or an alcohol. Removal of the catalyst residues can be omitted because the quantity of catalyst in the polymer, in particular the content of halogen and transition metal is very low now owing to the use of the catalyst system in the process according to the invention.

The presence of the diene in the EADM's prepared according to the process of the present invention makes it possible to vulcanize the EADM, generally in the form of a compound, with vulcanizing agents, as such known in the art. Suitable vulcanizing agents are e.g. peroxides, sulphur and sulphur containing compounds, phenolic resins.

The EADM's of the present invention can also be used in unvulcanized form, e.g. in blends with other polymeric products. They are useful in rubberized compounds. They are also useful in thermoplastic vulcanizates (blends of a plastic and an at least partially cured EADM).



The invention will now be elucidated by means of the following non-restrictive examples.

In the following: "Cp" means "cyclopentadienyl"; "Me" means "methyl"; "Bu" means "butyl".

5

#### EXAMPLES

##### Synthesis of bidentate monocyclopentadienyl complexes

###### 10 Example I

Synthesis of (dibutylaminoethyl)tetramethylcyclopentadienyltitanium(III) dichloride ( $\text{CpMe}_4(\text{CH}_2)_2\text{NBu}_2\text{TiCl}_2$ ).

###### 15 a. Preparation of ethyl 3-(N,N-di-n-butylamino)propionate

Ethyl 3-bromopropionate (18.0 g; 0.10 mol) was added carefully to di-n-butylamine (25.8 g; 0.20 mol), followed by stirring for 2 hours. Then diethyl ether (200 mL) and pentane (200 mL) were added. The precipitate was filtered  
20 off, the filtrate was boiled down and the residue was distilled at reduced pressure. The yield was 7.0 g (31%).

###### b. Preparation of bis(2-butenyl)(di-n-butylaminoethyl)-methanol

25 2-Lithium-2-butene was prepared from 2-bromo-2-butene (16.5 g; 0.122 mol) and lithium (2.8 g; 0.4 mol) as in example I. To this, the ester of a) (7.0 g; 0.031 mol) was added with reflux in approx. 5 minutes, followed by stirring for about 30 minutes. Then water (200 mL) was carefully added  
30 dropwise. The water layer was separated off and extracted twice with 50 ml of  $\text{CH}_2\text{Cl}_2$ . The combined organic layer was washed once with 50 mL of water, dried ( $\text{K}_2\text{CO}_3$ ), filtered and boiled down. The yield was 9.0 g (100%).

c. Preparation of (di-n-butylaminoethyl)tetramethyl-  
cyclopentadiene)

4.5 g (0.015 mol) of the carbinol of b) was added dropwise to 40 mL of concentrated sulphuric acid of 0°C, followed by stirring for another 30 minutes at 0°C. Then the reaction mixture was poured out in a mixture of 400 mL of water and 200 mL of hexane. The mixture was made alkaline with NaOH (60 g) while being cooled in an ice bath. The water layer was separated off and extracted with hexane. The combined hexane layer was dried ( $K_2CO_3$ ), filtered and boiled down. The residue was distilled at reduced pressure. Boiling point 110°C (0.1 mm Hg). The yield was 2.3 g (55%).

d. Preparation of (di-n-butylaminoethyl)tetramethylcyclo-  
pentadienylnititanium(III)dichloride

1.0 equivalent of n-BuLi (0.75 mL; 1.6 M) was added (after cooling to -60°C) to a solution of the  $C_5Me_4H(CH_2)_2NBU_2$  of c) (0.332 g; 1.20 mmol) in THF (50 mL), after which the cooling bath was removed. After warming to room temperature the solution was cooled to -100°C and then  $TiCl_3 \cdot 3THF$  (0.45 g; 1.20 mmol) was added in a single portion. After stirring for 2 hours at room temperature the THF was removed at reduced pressure. The purification was done as in Example I.

The catalysts given in Examples I and II were methylated with MeLi in diethylether.

Example II

The synthesis of [1,2,4-triisopropyl-3-(dimethylamino-  
ethyl)cyclopentadienyl]-titanium(III)dimethyl

a. Reaction of cyclopentadiene with isopropyl bromide

Aqueous KOH (50%; 1950 g; ca. 31.5 mol in 2.483 l water) and Adogen 464 (31.5 g) were placed in a 3 l three-neck flask fitted with a condenser, mechanical stirrer,

heating mantle, thermometer, and an inlet adapter. Freshly cracked cyclopentadiene (55.3 g; 0.79 mol) and isopropyl bromide (364 g; 2.94 mol) were added and stirring was begun. The mixture turned brown and became warm (50°C). The mixture was stirred vigorously over night, after which the upper layer containing the product was removed. Water was added to this layer and the product was extracted with hexane. The combined hexane layer was washed once with water and once with brine, and after drying (MgSO<sub>4</sub>) the solvent was evaporated, leaving a yellow-brown oil. GC and GC-MS analysis showed the product mixture to consist of diisopropylcyclopentadiene (iPr<sub>2</sub>-Cp, 40%) and triisopropylcyclopentadiene (iPr<sub>3</sub>-Cp, 60%). iPr<sub>2</sub>-Cp and iPr<sub>3</sub>-Cp were separated and isolated by distillation at reduced (20 mmHg) pressure. Yield: iPr<sub>2</sub>-Cp: 25% and iPr<sub>3</sub>-Cp: 40%.

b. Reaction of lithium 1,2,4-triisopropylcyclopentadienyl with dimethylaminoethyl chloride

In a dry 500 ml flask under dry nitrogen, containing a magnetic stirrer, a solution of 62.5 ml of n-butyllithium (1.6 M in n-hexane; 100 mmol) was added to a solution of 19.2 g (100 mmol) of iPr<sub>3</sub>-Cp in 250 ml of THF at -60°C. The solution was allowed to warm to roomtemperature (in approx. 1 hour) after which the solution was stirred over night. After cooling to -60°C, dimethylaminoethyl chloride (11.3 g; 105 mmol; freed from HCl (by the method of Rees W.S. Jr. & Dippel K.A. in OPPI BRIEFS vol 24, No. 5, 1992)) was added via a dropping funnel in 5 minutes. The solution was allowed to warm to roomtemperature after which it was stirred over night. The progress of the reaction was monitored by GC. After addition of water (and pet-ether), the organic layer was separated, dried and evaporated under reduced pressure. Next to the starting material iPr<sub>3</sub>-Cp (30%), 5 isomers of the product (dimethylaminoethyl)triisopropylcyclopenta-diene (LH;

70%) are visible in GC. Two isomers are geminal (together 30%). Removal of the geminal isomers was feasible by precipitation of the potassium salt of the  $i\text{Pr}_3\text{-Cp}$  anion and filtration and washing with pet-ether (3x). Overall yield 5 (relative to  $i\text{Pr}_3\text{-Cp}$ ) was 30%.

c. Applied reaction sequence to [1,2,4-triisopropyl-3-(dimethylaminoethyl)-cyclopentadienyl]titanium- (III)dimethyl

10 Solid  $\text{TiCl}_3 \cdot 3\text{THF}$  (18.53 g, 50.0 mmol) was added to a solution of  $\text{K}i\text{Pr}_3\text{-Cp}$  in 160 ml of THF at  $-60^\circ\text{C}$  at once, after which the solution was allowed to warm to roomtemperature. The color changed from blue to green.

Example III

15

a. Preparation of dimethylaminoethyl-tetraethylcyclopentadiene

20 In a Schlenk vessel equipped with a magnetic stirrer, a solution of tetraethylcyclopentadiene (2.066 g, 11.6 mmol, containing 15% geminal product) in 20 mL dry THF was introduced at room temperature. To this solution 6.00 mL of a solution of n-butyllithium in hexane (9.90 mmol) were added in a dropwise manner.

25 In another Schlenk vessel equipped with a magnetic stirrer, a solution of 9.74 mmol n-butyllithium in 5.90 mL hexane was added to a solution of 0.867 g (9.74 mmol) 2-dimethylaminoethanol in 35 mL THF that had been cooled to  $-78^\circ\text{C}$ .

30 After 2 hours of stirring at room temperature the mixture was cooled again to  $-78^\circ\text{C}$  and tosylchloride (1.855 g, 9.74 mmol) was added slowly in small portions. The mixture was brought to  $0^\circ\text{C}$  during 5 minutes of stirring. After 16 hours of stirring the conversion was 100% (28% geminal product).

b. Preparation of (dimethylaminoethyl)-tetra-  
ethylcyclopentadienyldtitanium(III)dichloride

In a Schlenk vessel 0.38 g (1.523 mmol) tetraethylcyclopentadienyldimethylaminoethyl was dissolved in 20 mL diethylether. The solution was cooled to -60°C. 0.95 mL 1.6 M butyllithium was added dropwise. After 30 minutes the cooling was stopped and the reaction was completed during one hour of stirring.

In a second Schlenk vessel 0.57 g (1.538 mmol)  $\text{TiCl}_3 \cdot \text{THF}$  was slurried in 30 mL THF. Both Schlenk vessels were cooled to -60°C and the anion-solution was added to the  $\text{TiCl}_3$ -slurry. A green suspension was obtained. The reaction mixture was brought slowly to room temperature. The reaction mixture was stirred overnight. Then the solvent was evaporated. The residue was a green solid that was analysed by mass spectroscopy and was found to be the title compound.

Analysis of the polymers

The composition of the terpolymers was determined with the aid of Fourier Transform Infrared Spectroscopy (FT-IR). The FT-IR results indicate the composition of the various monomers in weight percentages relative to the overall composition.

The intrinsic viscosity (IV) was determined in decaline at 135°C.

Example IV

400 ml of pentamethylheptane (PMH), 5 ml ethylidene norbornene (ENB) and  $3 \cdot 10^{-5}$  mol trioctylaluminum were introduced into a 1.5-litre reactor. The reactor was conditioned by passing a propylene-ethylene mixture over it. The propylene:ethylene ratio was 1. The reactor pressure was 0.8 MPa.

When the temperature and the off-gas of the reactor were constant,  $5 \cdot 10^{-6}$  mol of the catalyst, prepared in

Example I,  $3 \cdot 10^{-5}$  mol of dimethylanilinium tetrakis pentafluorophenyl borate and 100 ml of PMH were pumped into the reactor, which caused the polymerisation reaction to start. During the polymerisation the reactor's gas cap was  
5 refreshed with a stream of propylene-ethylene (100 nl and 100 nl, respectively).

After 10 min reaction time the pressure in the reactor was relieved and the clear solution was drained from the reactor. The polymer was isolated from the solution  
10 through evaporation.

A terpolymer of ethylene, propylene and ENB has been obtained. The polymer contained 49 wt% propylene and 9 wt% ENB. The intrinsic viscosity of the polymer was 1.29. The activity of the catalyst system was 1440 kg EPDM/mol  
15 transition metal \* 10 min.

#### Examples V-VI

The process of the present invention can also be applied for the preparation of ethylene/styrene/diene  
20 terpolymers (ESDM's), as shown in the following Examples.

Styrene was vacuum distilled over  $\text{CaH}_2$ . 600 ml of a dry alkane solvent (boiling range 65-70°C at 100 kPa pressure) was introduced into a 1.5 l stainless steel reactor. 45 g dried styrene was introduced in the reactor,  
25 followed by 3 ml dried 1,7-octadiene. Then the reaction mixture was heated to 80°C under an ethylene pressure of 800 kPa, followed by an equilibration period under stirring.

#### Example V

30 In a catalyst dosing vessel with a volume of 100 mL, 25 mL of the same solvent as present in the reactor was introduced at room temperature, followed by 20 mmol MAO (on Al-basis, Methyl Aluminoxane by Witco, 10 weight % in toluene) and 10 micromoles of the transition metal complex of  
35 Example II.

- After one minute of mixing, the catalyst/co-catalyst mixture was introduced into the reactor, thus starting the polymerisation reaction. The polymerisation was performed isothermally. After 6 minutes of polymerisation the
- 5 reaction was stopped, the reaction mixture drained from the reactor, followed by quenching with methanol. The polymer was stabilised using 1000 ppm of Irganox 1076® as anti-oxidant and was dried during 24 hours under vacuum at 70°C.
- 10 The polymer was analysed using  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR and was found to contain 1.6 mol% styrene and 0.6 mol% octadiene. The ESDM yield was 12,000 kg/mol transition metal \* hour.

#### Example VI

- 15 A polymerisation was performed under the conditions described in Example V but using the transition metal complex of Example III. The polymer was found to contain 3.5 mol% styrene and 0.5 mol% octadiene; the ESDM yield was 860 kg/mol transition metal \* hour.

20

Table 1 Examples of transition metal complexes useful in the invention  
(see formulas I-VI)

Me	L	Y	R	D	R'	K
Ti	Cl	C <sub>5</sub> H <sub>4</sub>	dimethylsilyl	N	methyl	L
Zr	F	C <sub>5</sub> Me <sub>4</sub>	diethylsilyl	P	ethyl	Y-R'
Hf	Br	Indenyl	dipropylsilyl	As	propyl	X
V	I	Fluorenyl	dibutylsilyl	Sb	n-butyl	diethyl ether
Nb	methyl	benzofluorenyl	methylamido	O	n-pentyl	tetrahydrofuran
Ta	methoxy	octahydrofluorenyl	dimethylgermanyl	S	methoxy	trimethylamine
Cr	ethoxy	C <sub>5</sub> H <sub>3</sub> (N-Bu)	diethylgermanyl	Se	ethoxy	triethylamine
Mo	hydride	tetrahydroindenyl	diethylpropylene		Cl	trimethylphosphine
W	isopropyl	C <sub>5</sub> H <sub>3</sub> (SiMe <sub>3</sub> )	tetramethyldisiloxane		F	triethylphosphine
	octyl	methylamido	diphenylsilyl		Br	triphenylphosphine
	propoxy	phenylphosphido	tetramethylsilaethylene		I	dimethylsulphide
	phenoxy		methylene		phenoxy	dimethylaniline
	benzyl		diethylmethylene		benzyl	
	methylthio		ethylene		H	
			dimethylethylene			
			ethylphosphido			
			phenylphosphido			

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10

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C L A I M S

What is claimed is:

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1. A process for the preparation of a terpolymer having an ethylene content of between 20 and 90 weight %, a diene content of up to 30 weight %, and an  $\alpha$ -olefin, comprising conducting polymerization of ethylene, one  
10 or more  $\alpha$ -olefins, and one or more dienes at a temperature between about  $-10^{\circ}\text{C}$  and about  $220^{\circ}\text{C}$  in the presence of a catalyst comprising a reduced transition metal complex and a co-catalyst, wherein said reduced transition metal complex has the  
15 following structure:



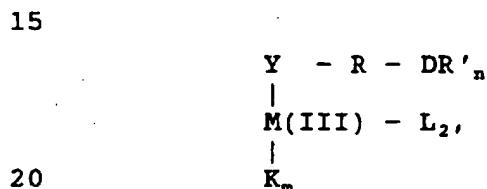
wherein:

- 25 M is a reduced transition metal selected from group 4, 5 or 6 of the Periodic Table of the Elements;
- X is a multidentate monoanionic ligand represented by the formula  $(\text{Ar}-\text{R}_t-)_s\text{Y}(-\text{R}_t-\text{DR}'_n)_q$ ;
- 30 Y is a member selected from the group consisting of a cyclopentadienyl, amido  $(-\text{NR}'-)$ , and phosphido  $(-\text{PR}'-)$  group;
- R is at least one member selected from the group consisting of (i) a connecting group between the Y group and the  $\text{DR}'_n$  group and (ii) a connecting  
35 group between the Y group and the Ar group, wherein when the ligand X contains more than one R group, the R groups can be identical as or different from each other;

- D is an electron-donating hetero atom selected from group 15 or 16 of the Periodic Table of Elements;
- 5 R' is a substituent selected from the group consisting of a hydrogen, hydrocarbon radical and hetero atom-containing moiety, except that R' cannot be hydrogen when R' is directly bonded to the electron-donating hetero atom D, wherein when the multidentate monoanionic ligand X
- 10 contains more than one substituent R', the substituents R' can be identical or different from each other;
- Ar is an electron-donating aryl group;
- 15 L is a monoanionic ligand bonded to the reduced transition metal M, wherein the monoanionic ligand L is not a ligand comprising a cyclopentadienyl, amido ( $-NR'-$ ), or phosphido ( $-PR'-$ ) group, and wherein the monoanionic ligands L can be identical or different from
- 20 each other;
- K is a neutral or anionic ligand bonded to the reduced transition metal M, wherein when the transition metal complex contains more than one ligand K, the ligands K can be identical or
- 25 different from each other;
- m is the number of K ligands, wherein when the K ligand is an anionic ligand m is 0 for  $M^{3+}$ , m is 1 for  $M^{4+}$ , and m is 2 for  $M^{5+}$ , and when K is a neutral ligand m increases by one for each
- 30 neutral K ligand;
- n is the number of the R' groups bonded to the electron-donating hetero atom D, wherein when D is selected from group 15 of the Periodic Table of Elements n is 2, and when D is selected from
- 35 group 16 of the Periodic Table of Elements n is 1;
- q and s are the number of ( $-R_c-DR'_n$ ) groups and

(Ar-R<sub>t</sub>-) groups bonded to group Y, respectively, wherein q + s is an integer not less than 1; and  
 t is the number of R groups connecting each of (i) the Y and Ar groups and (ii) the Y and DR'<sub>n</sub> groups, wherein t is selected independently as 0 or 1.

2. A process according to claim 1, wherein the Y group is a cyclopentadienyl group.
3. A process according to claim 2, wherein the cyclopentadienyl group is an unsubstituted or substituted indenyl, benzoindenyl, or fluorenyl group.
4. A process according to claim 2, wherein said reduced transition metal complex has the following structure:



wherein:

M(III) is a transition metal from group 4 of the Periodic Table of the Elements in oxidation state 3+.

5. A process according to claim 2, wherein said reduced transition metal is titanium.
6. A process according to claim 2, wherein said electron-donating hetero atom D is nitrogen.
7. A process according to claim 2, wherein the R' group in the DR'<sub>n</sub> group is an n-alkyl group.
8. A process according to claim 2, wherein said R group has the following structure:



wherein p is 1, 2, 3, or 4.

9. A process according to claim 2, wherein said monoanionic ligand L is selected from the group

consisting of a halide, an alkyl group, and a benzyl group.

10. A process according to claim 2, wherein the Y group is a di-, tri- or tetraalkyl-cyclopentadienyl.
- 5 11. A process according to claim 2, wherein said co-catalyst comprises a linear or cyclic aluminoxane or a triaryl borane or tetraaryl borate.
12. A process according to claim 2, wherein at least one member selected from the group consisting of said  
10 reduced transition metal complex and said co-catalyst is supported on at least one carrier.
13. The process according to claim 1, characterized in that said terpolymer has a number average molecular weight  $M_n$  of between 100 and 30,000, and the  
15 temperature at which the process is carried out is between about 30°C and about 220°C.
14. The process according to claim 1, characterized in that the polymerization is conducted at a temperature of between about 75°C and about 220°C.
- 20 15. The process according to claim 1, characterized in that the polymerization is conducted at a temperature of between about 135°C and about 220°C.
16. The process according to claim 1, characterized in that the  $\alpha$ -olefin is selected from the group of  
25 propylene, 1-butene, 1-hexene, styrene, ( $\alpha$ -methyl)styrene and 1-octene.
17. The process according to claim 16, characterized in that the  $\alpha$ -olefin is propylene or styrene.
18. The process according to claim 1, characterized in  
30 that the diene is selected from the group of dicyclopentadiene, ethylidene norbornene, vinylnorbornene, hexadiene, octadiene, isoprene, myrcene, allenes, isopropylidene tetrahydroindene, and mixtures thereof.

1/1

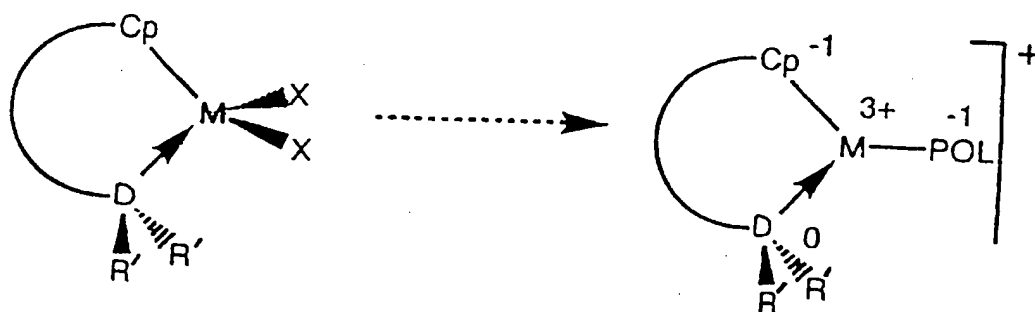


FIG. 1

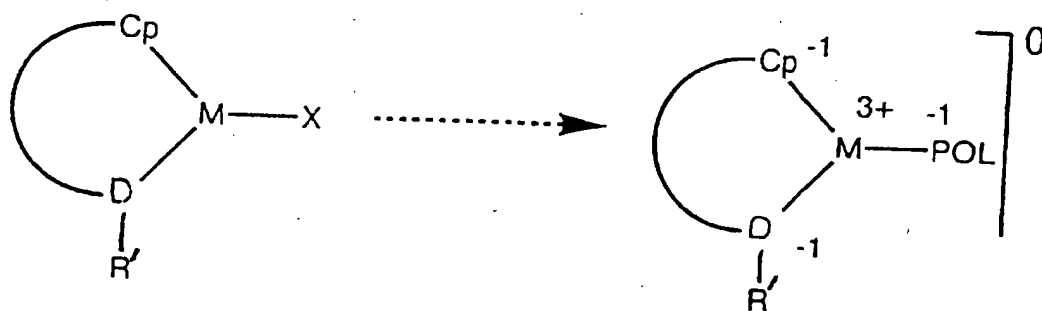


FIG. 2

# INTERNATIONAL SEARCH REPORT

Intern. al Application No.  
PCT/NL 97/00244

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08F210/18 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 96 13529 A (DSM NV ;BEEK JOHANNUS ANTONIUS MARIA V (NL); DOREMAELE GERARDUS HE) 9 May 1996 * claims; page 13, line 33 to page 14, line 4; page 15, lines 25-28; page 16, lines 4-15 *	1-18
A	WO 93 08221 A (DOW CHEMICAL CO) 29 April 1993 * claims; page 32, lines 3-11; page 32, line 23 to page 33, line 5 *	1-18
A	WO 93 19104 A (DOW CHEMICAL CO) 30 September 1993 * claims; page 12, lines 24-36 *	1-18
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "&" document member of the same patent family

Date of the actual completion of the international search

3 June 1997

Date of mailing of the international search report

26.06.97

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# INTERNATIONAL SEARCH REPORT

Internat'l Application No  
PCT/NL 97/00244

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP 0 347 129 A (EXXON CHEMICAL PATENTS INC) 20 December 1989 cited in the application * claims; page 2, lines 8-15 * -----</p>	1-18

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